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(54) RUBBER COMPOSITION AND METHOD FOR VULCANIZATION BONDING TO REINFORCING MATERIAL USING THE SAME

(57)Abstract:

PURPOSE: To obtain the composition, excellent in bonding performance in vulcanizing and bonding to a reinforcing material, having high hardness with hardly any deterioration in tensile properties and useful for vulcanization bonding of tires, etc., to the reinforcing material.

CONSTITUTION: The objective composition is obtained by blending (A) 100 pts.wt. rubber selected from natural rubber, styrene-butadiene copolymer rubber, butadiene rubber, isoprene rubber, acrylonitrile-butadiene copolymer rubber, chloroprene rubber and a (halogenated)butyl rubber with (B) 0.5-10 pts.wt. N,N'-m-phenylenebismaleimide, (C) 0.3-3 pts.wt. bi- or polyvalent carboximide or its anhydride and (D) 0.3-10 pts.wt. compound capable of emitting formaldehyde by heating. Furthermore, the component (C) is preferably a bivalent carboxylic acid anhydride and phthalic anhydride is especially preferably used. A condensate of melamine with formaldehyde and methanol is preferably used as the component (D).

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3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the rubber constituent in which it excels in the adhesive ability at the time of carrying out vulcanization adhesion with reinforcing materials in more detail about the rubber constituent, and a high degree of hardness is shown. this invention also relates to the tire manufactured from this rubber constituent, and the method of carrying out vulcanization adhesion with reinforcing materials using this rubber constituent again.

[0002]

[Description of the Prior Art] In the rubber goods which have the need of reinforcing with reinforcing materials, like a tire, a belt, and a hose, adhesion with rubber and reinforcing materials often poses a problem. Then, conventionally, the method of processing reinforcing materials with various adhesives, and the method of blending adhesives with other various compounding agents in the processing process of rubber are learned. The method of blending adhesives in the processing process of rubber also in these is widely adopted, in order not to be concerned with the existence of adhesives processing of reinforcing materials but to carry out vulcanization adhesion firmly.

[0003] It elaborates on this method and it is also called crowded type adhesion, the formaldehyde generating agent which generally generates formaldehyde by the formaldehyde acceptor and heating is blended with the rubber in a processing stage, and the unvulcanized rubber and reinforcing materials which are obtained are pasted up at the time of vulcanization. And there are a method using m-substitution phenols like a resorcinol or m-aminophenol, a method using the condensate of m-substitution phenols and the aldehydes like formaldehyde or an acetaldehyde, a method using the condensate to which other monochrome substitution phenols were made to react [phenols / m-substitution] with aldehydes, etc. as a formaldehyde acceptor.

[0004] The method using m-substitution phenols, especially a resorcinol as a formaldehyde acceptor was conventionally used widely from it being effective also in raising the degree of hardness of rubber among these. However, since the dispersibility of a resorcinol to rubber was bad, although it needed to knead at the elevated temperature, the resorcinol sublimated remarkably by elevated-temperature kneading, and it had become a big social problem -- it is not desirable on environmental hygiene. Furthermore, in the unvulcanized rubber which blended the resorcinol, the resorcinol carried out the bloom to the rubber front face, therefore it also had the fault of causing the adhesive fall between unvulcanized rubbers.

[0005] As a means to improve these faults, it is Japanese Patent Publication No. 45-27463 A number official report, JP,47-7640,B, U.S. ***** The condensate of a resorcinol and formaldehyde was proposed with the No. 2,746,898 specification etc. Although improvement of a grade which has set such so-called resorcinol resin to the dispersibility to rubber is found, since an unreacted resorcinol remained mostly in a resin, the problem by the evapotranspiration nature and the bloom of a resorcinol that an adhesive property was poor still remained. Furthermore, these resorcinol resins tended to deliquesce, therefore also had the problem on handling of solidifying during resin preservation.

[0006] Then, it is Japanese Patent Publication No. that the deliquescence of a resin and solidification nature should be improved. 52-26275 A number official report and Japanese Patent Publication No. 56-37902 The mixture which consists of a condensate of 3 component system copolycondensation object, and the resorcinol and formaldehyde which consist of a resorcinol, an alkylphenol, and formaldehyde, and a condensate of an alkylphenol and formaldehyde with a number official report etc. was proposed. these alkylphenol content resorcinol system resins are equivalent to the adhesive property and rubber physical properties which are acquired when the conventional resorcinol resin is used, or a thing which has the effect of it not less and improves the deliquescence which was the fault of the conventional resorcinol resin, and solidification nature However, also in these alkylphenols content resorcinol system resin, that sublimation of that is an environmental hygiene top problem, and since an unreacted resorcinol still remained to some extent, and an adhesive property with reinforcing materials and the degree of hardness of rubber were not necessarily still more enough, improvement of these faults was demanded strongly.

[0007]

[Problem(s) to be Solved by the Invention] That the fault which the well-known resorcinol resin and the alkylphenol content resorcinol system resin had should be solved in view of this situation, this invention persons came to complete this invention, as a result of repeating research variously.

[0008] Therefore, the purpose of this invention is to offer the rubber constituent with which it excels in vulcanization adhesive property ability with reinforcing materials, and the vulcanized rubber of a high degree of hardness is obtained.

[0009] Using a compounding agent without the deliquescence at the time of preservation, or solidification nature and the sublimability in a rubber kneading processing process, another purpose of this invention does not almost have the fall of machine physical properties, and is to offer a rubber constituent with a high degree of hardness.

[0010] The further purpose of this invention is to offer [offering the tire manufactured from this rubber constituent, and] the method of carrying out vulcanization adhesion with reinforcing materials using this rubber constituent.

[0011]

[Means for Solving the Problem] That is, this invention provides the rubber chosen from (A) natural rubber, a styrene butadiene rubber, butadiene rubber, polyisoprene rubber, acrylonitrile butadiene copolymerization rubber, chloroprene rubber, isobutylene isoprene rubber, and halogenation isobutylene isoprene rubber with the rubber constituent which comes to contain the compound which generates formaldehyde by N and N'-m-phenylene bismaleimide, the carboxylic acid more than (C) divalent or its anhydride, and (B) (D) heating.

[0012] this invention offers the method of carrying out vulcanization adhesion of rubber and the reinforcing materials by blending aforementioned component (B) - (D) with the aforementioned rubber (A), and vulcanizing under contact to reinforcing materials again.

[0013] The rubber (A) applied in this invention may be the blend object of two or more sorts of rubber, even if it is chosen out of natural rubber, a styrene butadiene rubber, butadiene rubber, polyisoprene rubber, acrylonitrile butadiene copolymerization rubber, chloroprene rubber, isobutylene isoprene rubber, and halogenation isobutylene isoprene rubber and consists of respectively independent rubber.

[0014] N [of a component (B)] and N'-m-phenylene bismaleimide is usually added in the range of 0.5 - 10 weight section to the rubber 100 weight section. This compound is preferably added in the range of per [0.5] rubber 100 weight section - 3 weight sections. The weight section of the combination component per following and rubber 100 weight section It expresses with the unit of phr.

[0015] As the carboxylic acid more than divalent [of a component (C)], or its anhydride, an aliphatic polycarboxylic-acid anhydride like an aliphatic polycarboxylic acid like a phthalic acid, an isophthalic acid, a terephthalic acid, trimellitic acid, a trimesic acid, aromatic polycarboxylic acids like a pyromellitic acid, phthalic anhydride, a trimellitic acid anhydride, an aromatic-polycarboxylic-acids anhydride like a pyromellitic-acid anhydride, oxalic acid, a maleic acid, a fumaric acid, an adipic acid, a sebacic acid, 1, 2 and 3, and 4-butane tetracarboxylic acid and a maleic anhydride etc. is mentioned, for

example. An acid anhydride, especially the anhydride of a divalent carboxylic acid are desirable, and phthalic anhydride is especially desirable. The addition of a component (C) is 0.3 - 3phr. It is a range. Under 0.3 phr is not enough for the loadings to raise the degree of hardness of rubber, and an adhesive property, and, on the other hand, they are 3phrs. Since vulcanization of rubber will be delayed remarkably and a curing time will become long if many, it becomes disadvantageous economically.

[0016] The compound which generates formaldehyde by heating which is another indispensable component (D) in this invention can be a formaldehyde generating agent usually used in rubber industry. That is, it is used with various formaldehyde acceptors like a resorcinol or a resorcinol system resin from the former. For example, a thing like the condensate of a thing like the condensate of a melamine and formaldehyde, i.e., a dimethylol melamine, trimethylolmelamine, a tetrapod methylol melamine, and a hexa methylol melamine, a melamine, formaldehyde, and a methanol, i.e., a hexa kiss (methoxymethyl) melamine, and a pentakis (methoxymethyl) methylol melamine and a further can apply a hexamethylenetetramine etc. Also in these, the condensate of a melamine, formaldehyde, and a methanol, i.e., methoxy-ized methylol melamine resin, is desirable. The loadings of a component (D) are 0.3 - 10phr. It is a range and is 1 - 6phr preferably. It is the range of a grade. The loadings are not so effective for adhesive ability with reinforcing materials, and the improvement in a degree of hardness of rubber at under 0.3 phr, and, on the other hand, are 10phrs. If it increases, since the elongation after fracture of rubber, the tensile strength before and behind heat aging, and the retention of tensile stress will fall remarkably, it is not desirable.

[0017] Such rubber (A) and component (B) The constituent containing - (D) is effective in especially vulcanization adhesion with reinforcing materials. The steel codes like nylon, rayon, polyester, the organic fiber like an aramid, the steel code that carried out brass plating, and the galvanized steel code as reinforcing materials to paste up are illustrated. Although what is necessary is just rubber reinforced with these either, of course, you may use two or more sorts of reinforcing materials.

[0018] Moreover, the rubber constituent of this invention can contain a bulking agent further if needed. Inorganic bulking agents, such as various kinds of things usually used in rubber industry as a bulking agent, for example, carbon black, and a silica, clay, a calcium carbonate, a glass fiber, are mentioned. Especially, from viewpoints, such as a degree of hardness of reinforcement nature or rubber, febrility, and dynamic endurance, especially a viewpoint of the degree of hardness of rubber, it is desirable to blend carbon black and the thing of the kind usually used in rubber industry, for example, SAF, ISAF, HAF, FEF, skin reactive factor, GPF, MT, etc. can be used. The loadings of a bulking agent, especially carbon black are 20 - 150phr. The range is desirable. Furthermore, apart from carbon black, it is also desirable to blend a water silica with carbon black for adhesive improvement. The loadings in the case of using a water silica have the desirable range of 5 - 40phr.

[0019] In this invention, it cannot be overemphasized again that the various rubber chemicals usually used in rubber industry, for example, an antioxidant, an antioxidant, an anti-ozonant, a vulcanizing agent, a cross linking agent, a vulcanization accelerator, a retarder, a ***** agent, a softener, a petroleum resin, lubricant, a plasticizer, a tackifier, etc. may be used together if needed.

[0020] They are especially a benzothiazole system vulcanization accelerator, for example, 2-mercaptobenzothiazole, and dibenzothiazyl. Since adhesive improvement is expected by blending and vulcanizing disulfide or N-alkylation benzo thiazyl sulfenamide, this benzothiazole system vulcanization accelerator is used preferably. The alkyl group replaced by N-grade in N-alkylation benzo thiazyl sulfenamide can be one piece or two pieces, and when two alkyl groups replace, it may form the ring, for example, a morpholine ring, with the nitrogen atom. The alkyl group replaced by N-grade can be annular [shape / of a straight chain / the letter of others and branching or annular]. As an example of N-alkylation benzo thiazyl sulfenamide, N-cyclohexyl-2-benzo thiazyl sulfenamide, N-t-butyl-2-benzo thiazyl sulfenamide, N-amyl-2-benzo thiazyl sulfenamide, N-oxy-diethylene-2-benzo thiazyl sulfenamide, N, and N-dicyclohexyl-2-benzo thiazyl sulfenamide etc. is mentioned. The loadings in the case of using a vulcanization accelerator, especially a benzothiazole system vulcanization accelerator are 0.1 - 4phr. The range is desirable.

[0021] Moreover, in adhesion with steel codes, for example, the steel code which carried out brass

plating, and the galvanized steel code, since adhesive improvement is expected by using together organic-acid cobalt, such as naphthenic-acid cobalt, this organic-acid cobalt is used preferably. The loadings in the case of using organic-acid cobalt are 0.1 - 1phr as an amount of cobalt. The range is desirable.

[0022] The rubber constituent of this invention blended in this way demonstrates the outstanding effect, when it applies to the member reinforced with the rubber goods of the various members of a tire, or others, especially reinforcing materials. For example, this rubber constituent is applied to a portion like a tire especially the bead section, or the carcass section reinforced with reinforcing materials, and a tire is manufactured through fabrication and a vulcanization process by the method usually performed in the tire industry.

[0023] In vulcanizing under contact to reinforcing materials, the suitable conditions which change with the kind of base rubber or kinds of various compounding agents are adopted. From the former, the vulcanization condition itself is adopted as general and it is not restricted [be / easy in this invention / especially / it].

[0024]

[Example] Next, this invention is not limited by these examples although this invention is explained in full detail with an example. Among the following examples, especially % and the section showing an addition or a content express weight % and the weight section, respectively, unless it refuses.

[0025] Examples 1 and 2. [0026]

[Table 1]

<Combination prescription> Natural rubber (ribbed-smoked-sheet#1) . 100 Section HAF Carbon Black (N330) 45 Section stearin acid 3 Section water silica (Nipsil AQ made from Japanese Silica Industry) 10 **** Lead Flower 5 Section antioxidant 2 Section (N-phenyl-N'-1, 3-dimethyl butyl-p-phenylene diamine)

Vulcanization accelerator The 0.7 sections (N and N-dicyclohexyl-2-benzo thiazyl sulfenamide)

** O U 2 Section N, N'-m-phenylene bismaleimide: Component (B) 1.5 section divalent carboxylic-acid system compound: Component (C) The 1.5 sections (phthalic anhydride (C1) or maleic anhydride (C2)) Methoxy-ized methylol melamine resin: Component (D) 4 Section (Sumikanol 507 by Sumitomo Chemical Co., Ltd.)

[0027] As a Banbury mixer, using Oriental Energy Machine factory 600ml lab plastic strike mill, based on the above-mentioned combination prescription, natural rubber, carbon black, stearin acid, a water silica, a zinc white, and an antioxidant are supplied at the oil bath temperature of 150 degrees C, and it is 50rpm. It kneaded for 15 minutes at the mixer rotational frequency (the first kneading process). The rubber temperature at this time was 155-170 degrees C.

[0028] Next, this compound was moved to the open mill, and N [of the vulcanization accelerator shown in the above-mentioned combination prescription, sulfur, and a component (B)] and N'-m-phenylene bismaleimide, the divalent carboxylic-acid system compound of a component (C), and the methoxy-ized methylol melamine resin of a component (D) were added and kneaded at the temperature of 50-70 degrees C (the second kneading process).

[0029] The examination of the MUNI scorching nature which shows a part of sample after kneading below was presented, the test piece which embedded the unsettled nylon code at the adhesive examination was created from the remaining samples, it vulcanized for 40 minutes at 145 degrees C with the vulcanizing press, and the adhesive examination shown below was presented. Moreover, to a **** physical-properties examination and hardness tests, the test piece was vulcanized for 40 minutes at 145 degrees C, and they were presented at the **** physical-properties examination and hardness test which are shown below. These test results were summarized in Table 2.

[0030] Per rubber compound before MUNI scorching sex-test vulcanization, and JIS K 6300 It was based and time until it goes up 5 point from the minimum value at the temperature of 125 degrees C was made into the scorching time.

[0031] About the adhesive property of the rubber constituent before adhesive test vulcanization, and an unsettled nylon code, it is ASTM D 2138. The H testing method of a publication estimated. used

unsettled nylon code 1890d/2 it is -- the average of 12 test pieces showed the result of an adhesion test [0032] **** physical-properties examination JIS K 6301 It is based, a dumbbell-like No. 3 test piece is used, and it is M300 as tensile strength, elongation after fracture, and tensile stress. It measured.

[0033] Hardness test JIS K 6301 It was based and the degree of hardness was measured with the spring formula hardness test (A type) using the right circular cylinder sample with 12.7mm [in thickness], and a radius of 14.5mm.

[0034] The example 1 of comparison. [0035] The same experiment as an example 1 was conducted except having not blended a component (B), (C), and (D). The result was shown in Table 2.

[0036] The examples 2 and 3 of comparison. [0037] a component (B) and (C) -- not using -- instead of -- the example 2 of comparison -- a resorcinol-formaldehyde resin (X) -- moreover -- the example 3 of comparison -- a resorcinol (R) -- each -- the same experiment as an example 1 was conducted 2 ***** except having blended with rubber at the first kneading process with carbon black etc., respectively The result was shown in Table 2.

[0038] In addition, the resorcinol-formaldehyde resin (X) used in the example 2 of comparison was manufactured as follows. Resorcinol 110g (1.0 mols) and 37% formalin 44.5g (0.55 mols) were taught to the 4 mouth flask which the reflux condenser and the thermometer attached, and it was made to react to it at 70 degrees C for 5 hours. Then, the reflux condenser was exchanged to the shunt, and the temperature up was carried out to 150 degrees C after decompressing to 25mmHg, it condensed for 3 hours, and the resorcinol-formaldehyde resin (X) with a softening temperature of 95 degrees C was obtained. The resorcinol content in a resin was 13.9%.

[0039] The examples 4-7 of comparison. [0040] The same experiment as examples 1 or 2 was conducted except having omitted a kind of a component (B), (C), and (D), or two sorts. The result was shown in Table 2.

[0041]

[Table 2]

| | 変動成分 * | スコーチ タイム (ML ₅) (分) | 接着 力 (kg) | 引 張 物 性 | | | 硬度 |
|-------|------------|--|-----------------|------------------------------------|-------------|--|----|
| | | | | 引張強さ (kgf/ cm ²) | 破断伸び (%) | M ₃₀₀ (kgf/ cm ²) | |
| 実施例 1 | B + C1 + D | 30.1 | 8.7 | 285 | 488 | 178 | 79 |
| " 2 | B + C2 + D | 26.5 | 8.6 | 280 | 478 | 176 | 78 |
| 比較例 1 | 無添加 | 22.1 | 3.6 | 286 | 496 | 150 | 66 |
| " 2 | X + D | 21.4 | 7.4 | 224 | 453 | 138 | 69 |
| " 3 | R + D | 14.6 | 6.5 | 285 | 489 | 163 | 77 |
| " 4 | B | 22.6 | 4.1 | 287 | 497 | 152 | 67 |
| " 5 | B + D | 21.6 | 6.6 | 281 | 500 | 150 | 71 |
| " 6 | B + C1 | 30.8 | 4.7 | 279 | 458 | 175 | 74 |
| " 7 | B + C2 | 27.6 | 4.4 | 274 | 468 | 173 | 73 |

* B: N and N'-m-phenylene bismaleimide C1: Phthalic anhydride C2: Maleic-anhydride D: Methoxy-ized methylol melamine resin X: Resorcinol-formaldehyde resin R: Resorcinol. [0042]

[Effect of the Invention] The rubber constituent of this invention shows a high degree of hardness, and is excellent in the point that there is also almost no fall of **** physical properties while it shows the adhesive ability which was excellent in vulcanization adhesion with reinforcing materials. Furthermore,

- the problem of the sublimability by the resorcinol which is the conventional adhesives, or the resorcinol which was the fault of a resorcinol system resin is also solved. Therefore, a quality product is obtained by applying this rubber constituent to the member reinforced with reinforcing materials, and performing vulcanization adhesion.

[Translation done.]